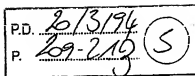XP-000943588

Simultaneous Determination of Diffusion Coefficient and Concentration by Chronoamperometry at a Microdisk Electrode

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Two unknown values among three electrochemical values, i.e. electrode area, diffusion coefficient, and concentration, are simultaneously obtained by nonlinear regression analysis of a single chronoamperometric faradaic current curve at a microdisk electrode. The approach is an analytical application of the semi-empirical equation presented by Shoup and Szabo for the chronoamperometric response at a disk electrode. To demonstrate the usefulness and accuracy of this approach, the chronoamperometric current at a platinum disk electrode of 50 μm radius in solutions of Ru(NH₃)₆³⁺, ferrocene, Fe(CN)₆³⁻, and C₆₀, were analyzed.

Introduction

The chronoamperometric response at a disk electrode has been studied for determination of the diffusion coefficient of electroactive species[1-4]. In most cases, at least two separate measurements and the approximate expressions for chronoamperometric current were used. In this study, two unknown parameters among diffusion coefficient (D), concentration (C), and electrode radius (a), are simultaneously determined from a single chronomperometric faradaic current at a disk electrode of small radius.

In general, the physicochemical unknowns are obtained by the endeavor to fit the experimental data with the proposed model. Therefore, if the equation for the model is proven to be accurate, it can be applied to obtain unknown values. The diffusion controlled chronoamperometric response at a disk electrode was solved by Ksenzhek et al.[5] and Aoki et al.[6,7]. The former describes the current function as an integral equation of the 1st order Bessel function and the latter describes that as a serial sum of Gamma function. The calculation itself of these functions may be challenging. Therefore, both are hardly applicable to fit the experimental data. A simple semi-empirical nonlinear equation which is accurate to 0.6% in arbitrary time domain was presented by Shoup and Szabo[8]. In the electrochemical experiment where 1% error is allowed, it may be regarded as a de facto solution.

In principle, since the accurate equation is known, it can be applied to the experimental data for the analytical purpose. It can be easily analyzed by the nonlinear curve fitting or the nonlinear regression analysis using ubiquitous personal computers in electrochemical laboratories, especially a computer with a data acquisition board. In the potential step experiment, the charging current is not negligible at the beginning time, but quickly (exponentially) decreases with time[9], i.e. $i_c \propto \exp(-t/(R_s C_d))$ where R_s is the solution resistance and C_d is the double layer capacitance. Therefore, the time domain for dominated faradaic current can be adjusted to fit the Shoup and Szabo equation which describes the faradaic current at a disk electrode. The time domain can be extended to very short time for the high concentration of electroactive species and electrolytes. For the arbitrary concentrated solutions, the chronoamperometric faradaic current should be obtained by the total current subtracted by non-faradaic current which can be approximated from the current in the same electrolyte solution without the electroactive species and in the same experimental conditions. In this work, the latter method is employed.

To demonstrate the usefulness and accuracy of the nonlinear regression approach, it is applied to the chronoamperometric faradaic current at a platinum disk electrode of 50 μm radius in various solutions. In result, we report values of diffusion coefficients of ferricyanide in aqueous solution,

ruthenium(III) hexaammine at pH 7.0 in aqueous solution, ferrocene in acetonitrile, and C_{60} in dichloromethane. The major goal in this study is the demonstration of the nonlinear regression approach by which two unknown values among three electrochemical values, i.e. electrode area, diffusion coefficient, and concentration, can be simultaneously determined when one of them is known. Note that the n value of electrode reaction, $O + ne \rightarrow R$, is assumed to be known throughout this work.

Theory

Considering the semi-infinite spherical diffusion for the electrode reaction, $O + ne \rightarrow R$, the principle of a new method can be easily understood because the equation is simple and linear. The chronoamperometric current[9] at a sphere electrode is as follows.

$$i(t) = nFADC^*/r_s + nFADC^*/(nDt)^{1/2}$$
$$= nF4\pi r_s DC^* + nF4\pi^{1/2} r_s^2 D^{1/2} C^* t^{-1/2} \quad (1)$$

, where A is the area of electrode, n is the number of electrons transferred per molecule, F is the Faraday constant, r_s is the radius of spherical electrode, D is the diffusion coefficent, C^* is the bulk concentration of the electroactive species, and t is the elapsed time since the potential step is applied. As mentioned above, the n value is assumed to be known. In equation (1), $i(t)$ is a linear function of $t^{-1/2}$. A plot of current versus $t^{-1/2}$ has the following slope and intercept:

$$slope = nF4\pi^{1/2} r_s^2 D^{1/2} C^*$$
$$intercept = nF4\pi r_s DC^*$$

Thus, two of n, r_s, D, and C^*, can be simultaneously determined from a single chronoamperometric curve, where two of them is known. H. Ikeuchi *et al.*[9] used this approach to determine the diffusion coefficients of several metal ions in aqueous solutions with a hanging mercury drop electrode.

The chronoamperometric response at a disk electrode in an infinite insulating plane is accurately (0.6% error) described by a simple semi-empirical equation which is presented by Shoup and Szabo.

$$i = 4nFDC^*a[A_1 + A_2\tau^{-1/2} + A_3 exp(-A_4\tau^{-1/2})] \quad (2)$$

, where $\tau = 4Dt/a^2$ and a is the radius of disk electrode. A_1, A_2, A_3, and A_4 are constant numeric values, $A_1 = \pi/4$, $A_2 = \pi^{1/2}/2$, $A_3 = 1 - \pi/4$, and $A_4 = (\pi^{1/2}/2 - 4\pi^{-3/2})/(1-\pi/4)$. The current at a disk embedded in an insulator is similar to that at a sphere electrode because both approach to a nonzero steady-state current at infinite time (or $t^{-1/2} \to 0$) while the theoretical steady-state current at a plane electrode or a shielded disk electrode should be zero (Figure 1(A)). The direct comparison of currents at a sphere and disk of same radius is unfair because the surface areas are different. By this reason, a quasi-hemisphere electrode of arbitrary solid angle, θ, is imaginatively designed. Note that the solid angle of full sphere is 4π and that of hemisphere is 2π. The conditions to determine the solid angle are that the surface area (A) and the steady-state current (i_{ss}) of a quasi-hemisphere electrode are same as those of a disk electrode, i.e.
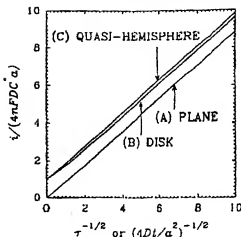

Figure 1. Chronoamperometric response at three different electrodes. $i/(4nFDC^*a)$ versus $\tau^{-1/2}$. (A) Current at a shielded disk electrode of radius a or at a plane electrode of πa^2 area, cottrell equation[9]. (B) Current at a disk electrode of radius a, Shoup and Szabo equation[8]. (C) Current at a quasi-hemisphere electrode of radius $(\pi/4)a$ and $16/\pi$ solid angle[11].

$$A = \theta r_s^2 = \pi a^2 \quad (3)$$
$$i_{ss} = nFDC^*\theta r_s = 4nFDC^*a \quad (4)$$

From the above two conditions,

$$r_s = (\pi/4)a \quad (5)$$
$$\theta = 16/\pi \quad (6)$$

In result, the currents at a disk electrode (Figure 1(B)) and a quasi-hemisphere electrode of $16/\pi$ (or 1.6211π) solid angle (Figure 1(C)) are very similar throughout all time domain with 6% relative deviation[11].

Since the chronoamperometric response at a disk electrode is similar to that of a quasi-hemisphere electrode, where $r_s = (\pi/4)a = 0.7854a$, and solid angle $= 16/\pi = 1.6211\pi$, the same strategy can be applied to the analysis of a disk electrode. One minor difficulty comes from that the theoretical current at a disk electrode is nonlinear against $t^{-1/2}$. A semi-empirical equation presented by Shoup and Szabo[8] is simple but still nonlinear. Thus, the chronoamperometric current at a disk electrode can not be analyzed from approach used by H. Ikeuchi *et al.*[9]. In this case, it can be analyzed by the nonlinear regression analysis. Theoretically, several parameters can be obtained from the nonlinear regression analysis. But, since the equation (2) closely resembles the current at a quasi-hemisphere electrode, practically two parameters can be obtained. For the nonlinear regression analysis, the algorithm, which is well described in the textbooks[12,13], is employed. The computer coding of this algorithm is constructed by C-language and compiled by Turbo-C 3.0. Since the procedure is well described in refences 12 and 13, the detailed description is omitted. In brief, the problem, is to find the best values of D, C^* and a, to fit the experimental data curve (current versus time) in the appropriate time domain. Starting with the initially guessed values of D, C^*, and a, the better guessed values to minimize the chi-square

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merit function[13] are found. The procedure is repeated until chi square merit function stops decreasing.

Experimental

All chemicals were used as received from commercial sources except for C_{60} which was obtained by the purification of soot produced in plasma discharge of graphite rod[14,15]. The supporting electrolyte of ferrocene (Aldrich Chemical Co., Inc.) was 0.1 M tetraethylammonium perchlorate (BAS, Inc.) in acetonitrile (Merck). For potassium ferricyanide (Sigma Chemical Co.), the supporting electrolyte was 1.0 M KCl (Aldrich Chemical Co., Inc.). The supporting electrolyte for ruthenium hexaamine trichloride (Aldrich Chemical Co., Inc.) was 0.1 M Na_2HPO_4 (Junsei Chemical Co., Ltd.) adjusted to pH 7.0 with phosphoric acid. For C_{60}, the supporting electrolyte was 0.1 M tetrabutylammonium tetrafluoroborate (Aldrich Chemical Co., Inc.) in dichloromethane (Junsei Chemical Co., Ltd.). All solutions were deoxygenated by argon bubbling prior to measurements. Aqueous solutions were prepared with triply distilled water.

A conventional three electrode system with one compartment cell was used for all measurements. A platinum wire (0.5 mm diameter and *ca.* 5 cm length) was used as a counter electrode. A platinum disk electrode of 50 μm radius (BAS, Inc.) was used as a working electrode. As a reference electrode, a saturated calomel reference electrode(SCE) was used for aqueous systems and a silver quasi-reference electrode (Ag-QRE) was used for nonaqueous systems. In this work, electrode was polished with 0.05 μm alumina solution or sequentially 6 μm, 3 μm, and 1 μm diamond paste, and used in 5 to 10 chronoamperometric experiments.

For the cyclic voltammetry and chronoamperometry, a homemade potentiostat, which is interfaced to a personal computer (NCS-386S System, Newcom System Co., Korea) *via* a data acquisition card (12 bit A/D converter card, Model PCL-812, Advantech Co., Ltd., Taiwan), was used. The control program was constructed by C-language.

Results and Discussion

As mentioned above, the current at a disk (Figure 1(B)) is similar to a quasi-hemisphere electrode (Figure 1(C)). Both curves approach to nonzero intercepts at infinite time, while the current at a shielded disk electrode or planar electrode should approach to zero value. The nonlinearity of the current at a disk electrode can be exaggerated in the plot of $d(i/(4n FDC^*a))/d(\tau^{-1/2})$ versus $\log(\tau^{-1/2})$ as seen in Figure 2.

The chronoamperometric faradaic current was obtained by the total current subtracted by non-faradaic current which can be approximated from the current in the same electrolyte solution without the eletroactive species and in the same experimental conditions. For the time domain to be analyzed, in general, the following two factors should be considered. One is the instrumental error and the other is the size of electrode. First of all, because of the data acquisition system of 5 KHz in this work, the time region of less than 1 msec is not possible. Also, the RC time constant in the current-voltage converter (100 nA/Volt) forces to discard data at short time. In this work, the fixed feedback system of the fixed RC time constant is measured as $9(\pm 1)$ msec using
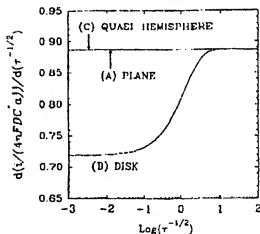

Figure 2. A plot of $d(i/(4n FDC^*a))/d(\tau^{-1/2})$ *vs.* $\log(\tau^{-1/2})$ for the chronoamperometric response. (A) Current at a shielded disk elertrode of radius *a*. (B) Current at a disk electrode of radius *a*. (C) Current at a quasi-hemisphere electrode of ($\pi/4$)*a* and $16/\pi$ solid angle.

a dummy cell. Therefore, the current data after the 5 times of this is in less than 1% error[8]. In result, the shortest time with this instrument is 50 msec. On the other hand, if the current data are acquired only at the longer time region, then the variations of current and $t^{-1/2}$ is so small to be alike a point data in the plot of i versus $t^{-1/2}$. In numerous trials, it is found that the optimum time domain for the nonlinear regression analysis is in $\tau^{-1/2}=0.3$ to 2.5, when the current curve is distinctively nonlinear as seen in Figure 2. But, the data before 50 msec has to be rejected to avoid the instrumental error as mentioned above. For example, when the radius of disk is 50 μm and the diffusion coefficient is 6.5×10^{-5} cm^2/sec as a typical value, the real time domain is in the range of 0.2 to 14 sec. But, in the case of 5 μm radius, the real time domain is in the range of 2 to 140 msec. The current voltage converter of 10 times higher sensitivity with decreased RC time constant is mandatory. Therefore, the platinum disk electrode of 50 μm radius was employed in this work. The larger disk electrode of 1 mm diameter can be employed. In this case, the vibrational problem has to be considered, because the time domain has to be extended to 1400 sec without disturbing the larger diffusion length $(2D/t)^{1/2}=1.2$ mm.

The half-wave potential is determined by cyclic voltammetric curves as listed in Table 1. For the diffusion controlled chronoamperometry, the initial potential is selected as far negative from its half-wave potential for oxidation (or far positive for reduction) and the step potential is selected as far positive for oxidation (or far negative for reduction). These potential values are listed in Table 1. In this way, the step potentials can be unambiguously selected for the organic solvent system where the unreliable Ag-QRE is used.

The typical curve fitting results of the nonlinear regression analysis are shown in Figure 3. All the experimental results are excellently fitted to the theoretical curve. The numerical results of nonlinear regression for $Ru(NH_3)_6^{3+}$, ferrocene, and $Fe(CN)_6^{3-}$ are summarized in Table 2. First of all, the radius values are not much deviated from the specification value

Table 1. Half-wave Potentials for Four Electroactive Solutions and the Applied Potentials in Chronoamperometric Measurements

Solutions[a]	$E_{1/2}$(mV)	E_i(mV)[b]	E_s(mV)[c]	Reference electrode
(1) Ru(NH$_3$)$_6^{3+}$	−225[c]	0	−400	SCE
(2) Ferrocene	550[d]	300	800	Ag-QRE
(3) Fe(CN)$_6^{3-}$	230	500	0	SCE
(4) C$_{60}$	340[c]	−500	−600	Ag-QRE

[a] (1) Ru(NH$_3$)$_6^{3+}$: 1.00 mM Ru(NH$_3$)$_6$Cl$_3$ in the aqueous solution of 0.1 M Na$_2$HPO$_4$, adjusted to pH=7.0 with phosphoric acid. (2) Ferrocene: 1.00 mM ferrocene in acetonitrile solution of 0.1 M tetraethylammonium perchlorate. (3) Fe(CN)$_6^{3-}$: 4.00 mM K$_3$Fe(CN)$_6$ in the aqueous solution of 1.0 M KCl. (4) C$_{60}$: C$_{60}$ in dichloromethane solution of 0.1 M tetrabutylammonium tetrafluoroborate. [b] E_i is initial potential before potential step to E_s. [c] Scan rate=305 mV/s. [d] Scan rate=610 mV/s.
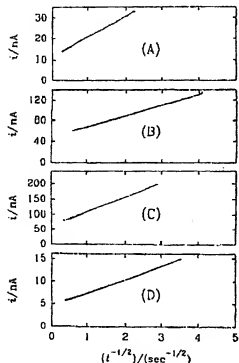
Figure 3. Comparison of experimental current (●) and theoretical current (—). (a) Ru(NH$_3$)$_6^{3+}$. (b) ferrocene. (c) Fe(CN)$_6^{3-}$. and (d) C$_{60}$. The sampling rate was 40 msec per point except for ferrocene where it was 20 msec. See Table 1 for the experimental conditions, i.e. solvent and electrolyte.

of BAS, Inc., 50 μm. The spread of data are less than ±0.9 μm for one electrochemical system, i.e. 49.9 to 50.5 μm in Ru(NH$_3$)$_6^{3+}$ system, 51.5 to 51.7 μm in ferrocene system, and 49.8 to 50.7 μm in Fe(CN)$_6^{3-}$ system. The radius measurement deviations between different systems was about 2%

Table 2. The Diffusion Coefficients (D) and Electrode Radii (a) Determined Simultaneously from Nonlinear Regression Analysis. Every Reported Result is the Average Value (D or a) of the Nonlinear Regression Analysis Results of at Least 5 Repetitive Chronoamperometric Curves with a Fresh Working Electrode Which Was Polished with Alumina Solution or Diamond Paste. Units : 10^{-5} cm^2/sec for D and 1 μm for a.

Solution[a] Experiment	Ru(NH$_3$)$_6^{3+}$[b]		Ferrocene[c]		Fe(CN)$_6^{3-}$[d]	
	D	a	D	a	D	a
1	0.566	50.5	2.46	51.5	0.780	50.4
2	0.580	49.9	2.49	51.7	0.764	50.7
3	0.586	50.4	2.45	51.5	0.782	49.8
Average	0.577	50.3	2.47	51.6	0.775	50.3

[a] See Table 1. [b] Temperature = 28±0.5℃. Polished with 0.05 μm alumina solution. [c] Temperature = 25±0.5℃. Polished with 0.05 μm alumina solution. [d] Temperature = 27±0.5℃. Polished sequentially with 6 μm, 3 μm, 1 μm diamond paste.

lationship[9] was considered, i.e. the diffusion coefficient increases by 1 to 2% with increasing temperature. The diffusion coefficient value (D=0.577×10^{-5} cm^2/sec at 28℃) of Ru(NH$_3$)$_6^{3+}$ in Table 2 shows good agreement with that reported by Wightman et al.[3] (D=0.548×10^{-5} cm^2/sec at 25℃), assuming D value increases by 1.7% with temperature. The diffusion coefficient value (D=2.47×10^{-5} cm^2/sec at 25℃) of ferrocene in Table 2 also shows good agreement with the literature value (D=2.4×10^{-5} cm^2/sec at 22℃)[6], assuming D value increases by 1.0% with temperature. In the case of ferricyanide, the literature values of ferricyanide are scattered in broad range[16]. The diffusion coefficient value of Fe(CN)$_6^{3-}$ in Table 2 is in good agreement with those reported by von Stackelberg (D=0.763×10^{-5} cm^2/sec at 25℃)[19] and Adams (D=0.74×10^{-5} cm^2/sec at 25℃)[20], assuming D value increases by 0.8 or 2.3% with temperature, respectively. The former[19] reported the resulting same D values employing two different electrodes. One is the carefully constructed planar platinum electrode system which surely excludes the edge effect and the other was the dropping mercury electrode system (polarography). The latter[20] used the flow injection analysis technique which was non-electrochemical method. The D values of various methods, including the method in this work, are all in good agreements. But, the value (D=0.726×10^{-5} cm^2/sec at 25℃) obtained by thin-layer cell[18] seems measured low.

In the case of C$_{60}$ solution in dichloromethane, three parameter D, C^*, and a, are assumed to be all uncertain. To solve this problem, two step method is used. At first, the radius of electrode is determined from the nonlinear regression analysis of ferrocene solution system. The same electrode is immediately transferred to C$_{60}$ solution system to measure the chronoamperometric response. In this process, since the effective radius of electrode may change as a result of polishing, the electrode is not polished at all. Instead it was just rinsed with acetonitrile and dichloromethane and dried in the air. By this procedure, the results of nonlinear regression analysis of faradaic current for C$_{60}$ system are

Table 3. The Simultaneous Determined Diffusion Coefficient (D) and Concentration (C^*) of C_{60} from Nonlinear Regression Analysis. Every Reported Result is the Value (D, C^* or a) Calculated from the Nonlinear Regression Analysis of a Single Chronoamperometric Faradaic Curve. A Working Electrode Was Polished with 0.05 μm Alumina Solution. Units : 10^{-5} cm²/sec for D, 1 μm for a and 1 mM for C^*

Solution[a]	Ferrocene[b]		C_{60}^c		C_{60}^d		C_{60}^e	
Experiment	D	a	D	C^*	D	C^*	D	C^*
1	2.52	51.4	1.02	0.219	0.98	0.232	1.07	0.207
2	2.51	51.3	1.05	0.215	1.01	0.228	1.09	0.203
3	2.51	51.3	1.07	0.217	1.03	0.230	1.11	0.204
4	2.51	51.3	1.03	0.226	0.99	0.239	1.07	0.213
5	2.51	51.2	1.12	0.214	1.23	0.201	1.16	0.202
Average	2.51	51.3	1.06	0.218	1.05	0.226	1.10	0.206

[a] See Table 1. [b] Temperature $= 27 \pm 0.5$ ℃. [c] Temperature $= 25 \pm 1$ ℃. Assuming $a = 51.3$ μm. [d] Temperature $= 25 \pm 1$ ℃. Assuming $a = 50.3$ μm. [e] Temperature $= 25 \pm 1$ ℃. Assuming $a = 52.3$ μm.

μm in 95% confidence level). But, it has to be reminded that the error associated with the determination of electrode radius between two different systems is 2% as mentioned above. The radius of electrode is $a = 51.3 \pm 1.0$ μm. Using the minimum and maximum value of a, $D = (1.05 \pm 0.12) \times 10^{-5}$ cm²/sec and $D = (1.10 \pm 0.05) \times 10^{-5}$ cm²/sec in 95% confidence level. In the confidence level, D value of C_{60} is $(1.05 \pm 0.12) \times 10^{-5}$ cm²/sec. Diffusion coefficient of C_{60} in this work is about 2 times higher than that determined by Kadish *et al.*[21] using the rotating disk technique at 22 ± 1 ℃. However, considering the accuracy of this approach, the diffusion coefficient reported by Kadish *et al.* seems to be measured lower.

Conclusion

Two of the three parameters D, C^*, and a, are simultaneously determined from a single chronoamperometric faradaic current curve at a microdisk electrode. It is demonstrated that this approach can be consistently applied to any electrochemical systems with less than 2% error. This approach can be helpful in numerous analytical situations, especially when the standard curve cannot be obtained. Even when all the electrochemical parameters are unknown, a couple of chronoamperometric experiments lead to the determinate results of D, C^* and a. Most importantly, the diffusion coefficient can be precisely obtained without separate determination of the effective surface area which has to be carefully obtained by the system of precisely known D and C^* in the other electroanalytical method. In result, we reported the diffusion coefficients of four electroactive species. Among them, only the diffusion coefficient of C_{60} in dichloromethane shows the huge difference with the literature value, while

the other three are consistently in good agreements with the literature values. Therefore, we conclude that the diffusion coefficient of C_{60} obtained in this work is more reliable. The diffusion coefficient of C_{60} in dichloromethane is $(1.05 \pm 0.12) \times 10^{-5}$ cm²/sec in 95% confidence level.

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